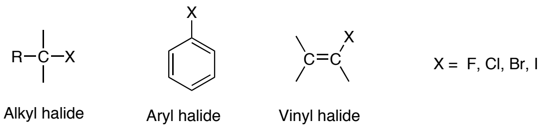
Chapter 10: **Alkyl Halides**

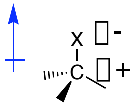


10.1 Naming alkyl halides- Read

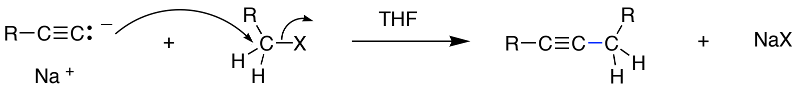
10.2 Structure of alkyl halides

Table 10.1

Halomethane	Bond length (pm)	Bond strength (KJ/mol)	Dipole Moment
H_3C-F	139	452	1.85
H_3C-Cl	178	351	1.87
H_3C-Br	193	293	1.81
H_3C-I	214	234	1.62

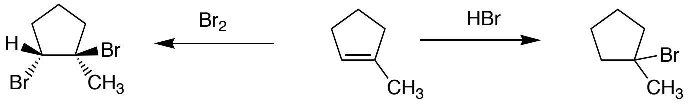


The significant dipole moment of alkyl halides make then good electrophiles for substitution reactions



Preparation of Alkyl Halides:

Electrophilic addition of HX and X_2 to alkenes (Chapter 6)



Free radical halogenation

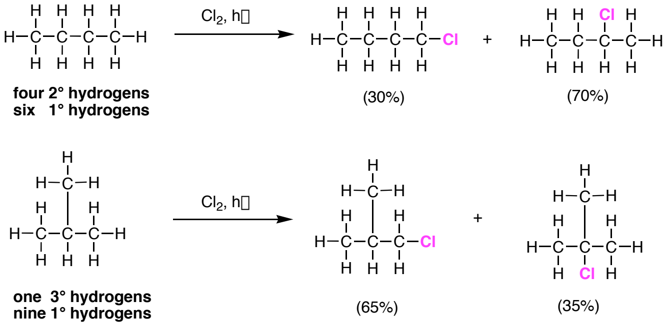
Mechanism of free radical halogenation (Chapter 5)

- three distinct steps
  1. Initiation
  2. Propagation
  3. Termination

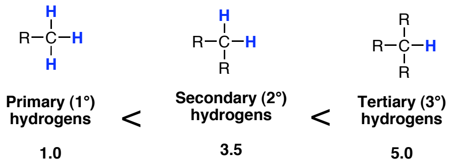
Free radical chlorination is not very useful for making alkyl chlorides

polychlorination

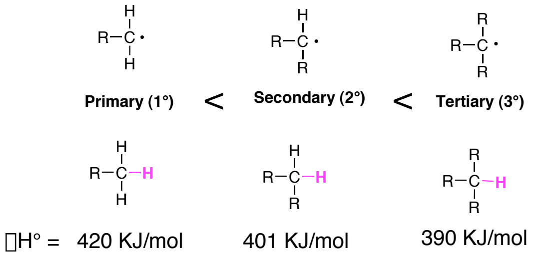
non-specific chlorination

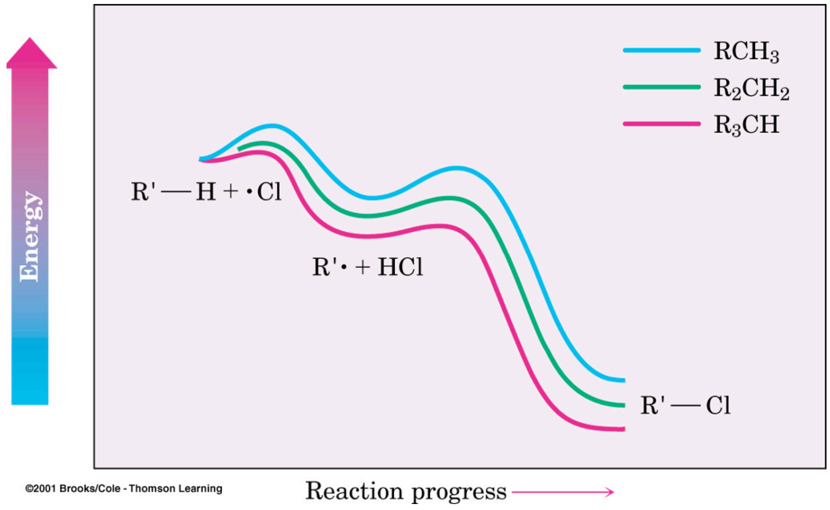


Relative reactivity of hydrogens toward free radical chlorination

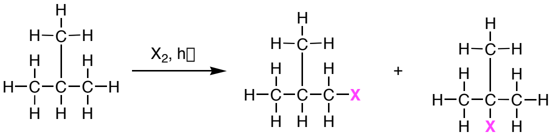


Reactivity is reflective of radical stability





Free radical bromination is much more selective for the most stable radical intermediate.



X = Cl 65 : 35
X = Br 1 : 99

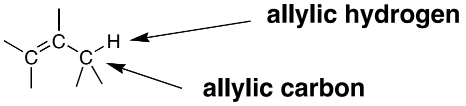
The propagation step for free radical bromination is endergonic, as opposed to chlorination which is exergonic. According to the Hammond postulate the transition state for bromination should resemble the product radical, and therefore be more selective for the product going through the more stable radical intermediate

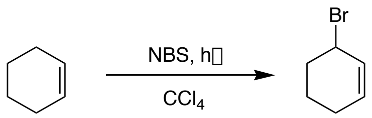
$$R_3C\text{-}H \quad + \quad X\bullet \quad \longrightarrow \quad R_3C\bullet \quad + \quad HX$$

X = Cl ΔH° = -50 KJ/mol
X = Br ΔH° = +12 KJ/mol

Allylic Bromination of Alkenes

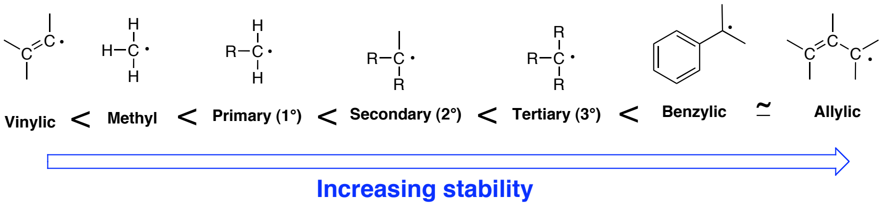
<u>allylic</u> position is the next to a double bond





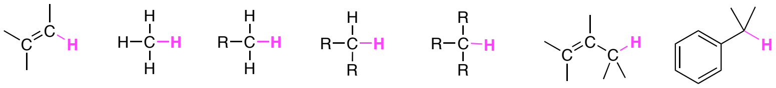
Allylic bromination of an alkene takes place through a free radical mechanism.

Radical Stability



Vinylic < Methyl < Primary (1°) < Secondary (2°) < Tertiary (3°) < Benzylic ≃ Allylic

Increasing stability



ΔH° (KJ/mol) = 444 438 420 401 390 361 368

Radicals are also stablized by hyperconjugation

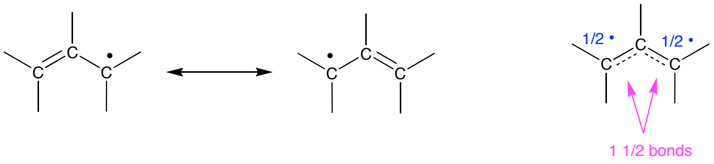
Allylic radical is resonance stabilized

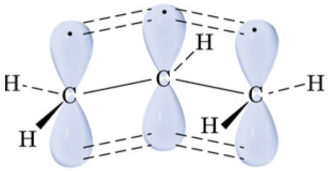
Recall (and please review) from Chapter 2:

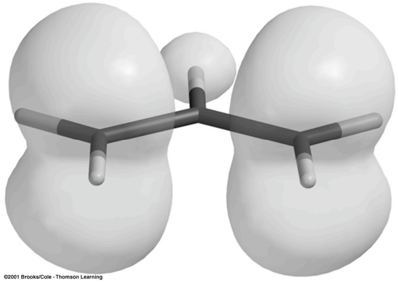
resonance forms- atoms remain fixed in all resonance forms. Resonance forms differ only by the placement of electrons

No one resonance form is entirely accurate. The actual structure is a hybrid of all the resonance forms. Resonance forms do not necessarily contribute equally to the resonance hybrid.

The greater the number of resonance structures the more stable the resonance hybrid.







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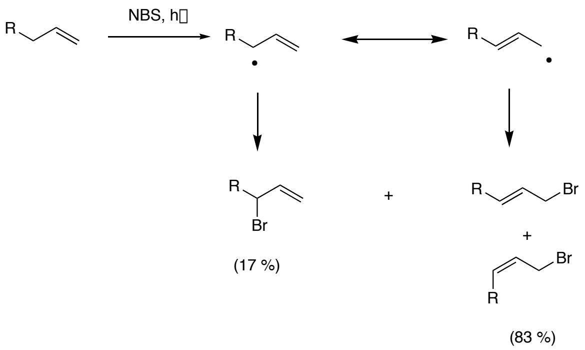
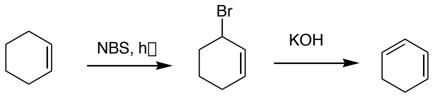
Map of the electron density due to the unpaired electron (the "spin")





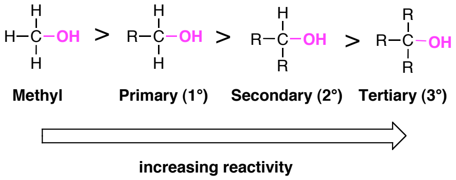
Alkyl halides from alcohols

the most general method of preparing alkyl halides

1. Substitution reaction of alcohols with HX

$$R\text{-}OH \quad + \quad HX \longrightarrow R\text{-}X \quad + \quad H_2O$$

Works better with more substituted alcohols



Polar mechanism with a carbocation intermediate. Reactivity reflects the stability of the carbocation intermediate (Chapter 11). One drawback to this method is that carbocations can rearrange.

2. Prepartion of alkyl chlorides by the treatment of alcohols with thionyl chloride ($SOCl_2$)

$$R\text{-}OH \quad + \quad SOCl_2 \longrightarrow R\text{-}Cl \quad + \quad SO_2 \quad + \quad HCl$$

3. Prepartion of alkyl bromides by the treatment of alcohols with Phosphorous tribromide (PBr_3)

$$R\text{-}OH \quad + \quad PBr_3 \quad \longrightarrow \quad R\text{-}Br \quad + \quad P(OH)_3$$

These methods work best on primary and secondary alcohols. They do not work at all for tertiary alcohols

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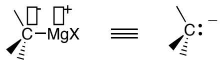
. . . more reactions of alkyl halides: Grignard reagents

Alkyl halides will react with some metals (M^0) in ether or THF to form organometallic reagents

Grignard reagent- organomagnesium

$$R\text{-}X \quad + \quad Mg^{(0)} \xrightarrow[\text{or THF}]{\text{ether}} R\text{-}Mg^{(II)}\text{-}X \qquad X = Cl, Br, I$$

R can be a variety of organic groups: 1°-, 2°-, 3°-alkyl, aryl or vinyl



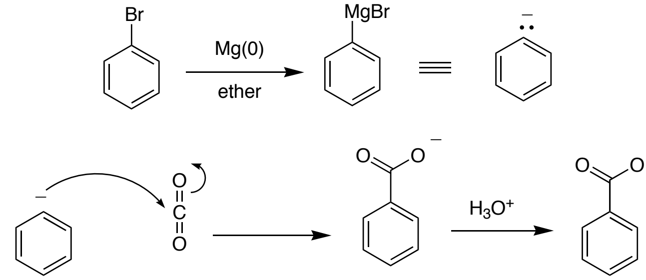
carbon nuccleophile
(recall acetylide anion)

Carbanions: nucleophile
react with electrophile

$$\text{R-X} \longrightarrow \text{R-MgX} \xrightarrow{H_2O} \text{R-H}$$

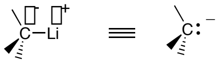
Grignard reagents are most commonly used in reactions with carbonyl compounds (Chapter 19).

Lab:



Organometallic coupling reactions:
organolithium reagents

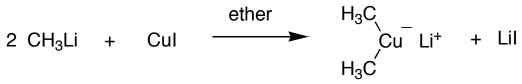
$$\text{R-X} \xrightarrow[\text{pentane}]{\text{Li}^{(0)}} \text{R-Li} + \text{LiX}$$



very strong bases
very strong nucleophiles

organolithium reagents are most commonly used as very strong bases and in reactions with carbonyl compounds

Cuprates (Gilman's reagent)



$$2\ CH_3Li + CuI \xrightarrow{\text{ether}} (H_3C)_2Cu^- \ Li^+ + LiI$$

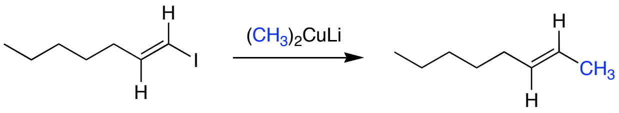
Gilman's reagent
(dimethylcuprate, dimethylcopper lithium)

R_2CuLi = R^- strong nucleophiles

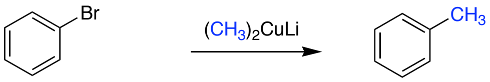
Nucleophilic substitution reaction with alkyl halides (alkylation)

$$CH_3(CH_2)_8CH_2\text{-}I + (CH_3)_2CuLi \xrightarrow{\text{ether}} CH_3(CH_2)_8CH_2\text{-}CH_3 + CH_3Cu + LiI$$

Reaction with vinyl and aryl halides



double bond geometry
is preserved



Oxidation [O]: the loss of electrons.

Decrease in electron density on carbon by forming a C-O, C-N, C-X bonds or by breaking C-H bonds

Increase in O, N, X content or decrease in H content

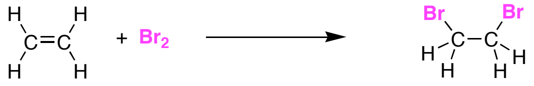
Reduction [H]: the gain of electrons

Increase in electron density on carbin by forming C-H bonds or breaking C-O, C-N, C-X bonds

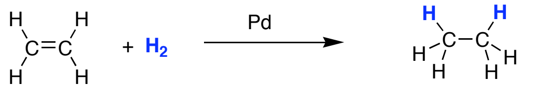
increase on H content or decrease in O, N, X content

$CH_4 + Cl_2 \longrightarrow H_3C\text{-}Cl$ oxidation

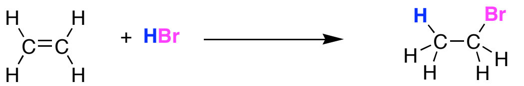
$H_3C\text{-}Cl \xrightarrow[2)\ H_3O^+]{1)\ Mg} CH_4$ reduction



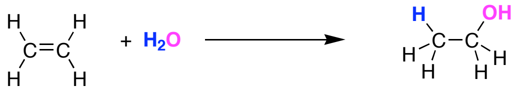
Oxidation



Reduction



Neither [O] or [H]



Neither [O] or [H] (hydration)

Table 10.5: Increasing oxidation state